Hydrogenation of Long Wavelength Infrared Focal Plane Arrays Based on Type II Superlattices

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Motivation and Opportunities

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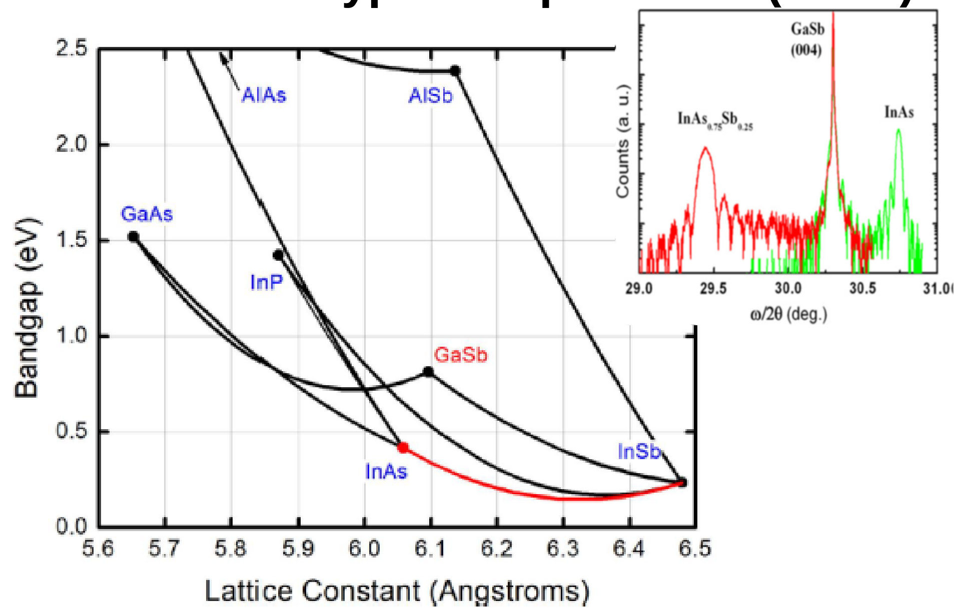
Requirements

- Broad spectral response
- Large format focal plane arrays (FPAs)
- Improved operability
- Higher sensitivity
- Higher operating temperature

Limitations

- Surface passivation problematic
- Longer wavelengths require higher Sb content, which adds strain
- Shockley-Read-Hall (SRH) lifetimes dominate below ~150 K
- Absorption coefficient in two-layer superlattices < HgCdTe

InAs/InAsSb Type 2 Superlattice (T2SL)



- GaSb substrates readily available
- May be strain-balanced for growth on GaSb substrates
- Broad spectral response (2-20 µm)
- Electron effective mass > HgCdTe: should reduce tunneling current
- Smaller Auger coefficient (longer Auger lifetime) than HgCdTe

Technical Background

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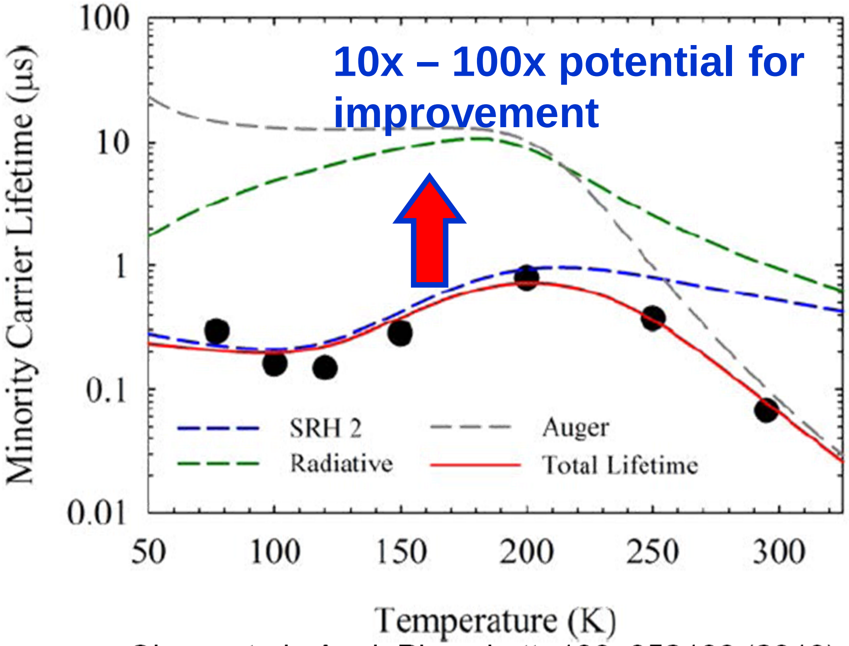
Key Material Properties

- Minority carrier lifetime
- Minority carrier diffusion length
- Absorption

- Dark current
- Noise
- Spectral response
- QE

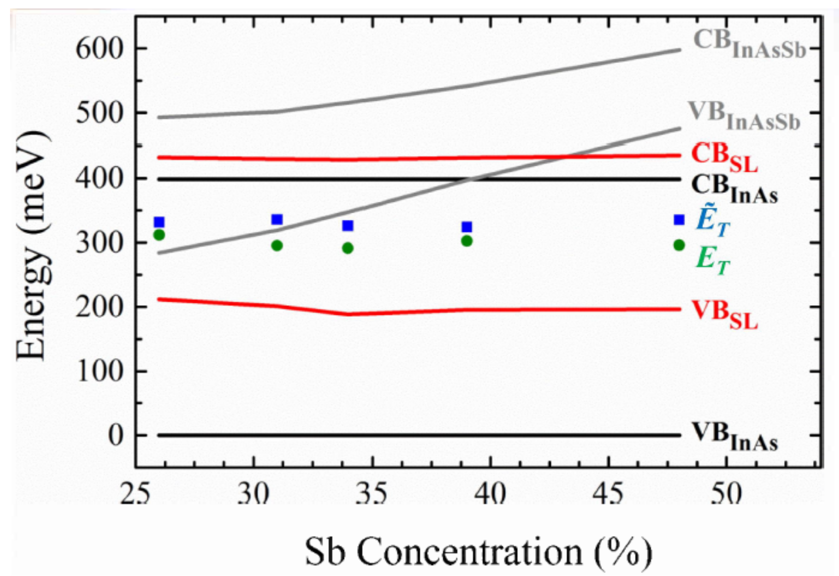
- Sensitivity
- Detectivity
- Operating temperature

T2SL carrier lifetime: ~10 µs, 100 – 200 K
Limited by SRH (defects)



Olson, et al., Appl. Phys. Lett. 103, 052106 (2013)

InAs/InAsSb defects create mid-gap states

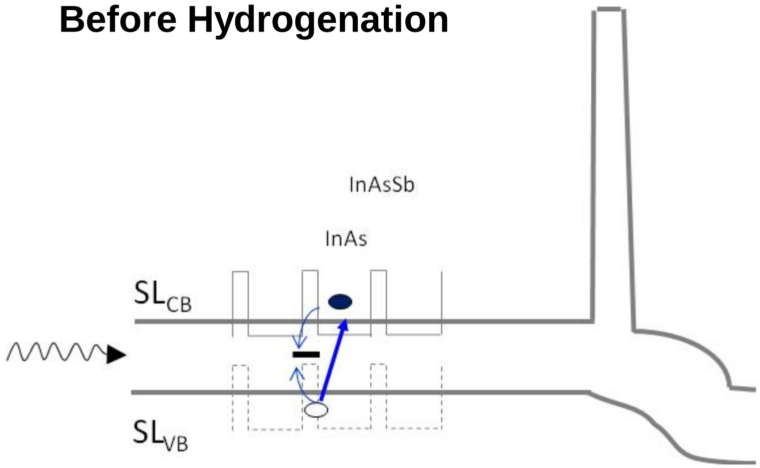


Aytac, et al., Appl. Phys. Lett. 105, 022107 (2014)

Effects of Hydrogenation

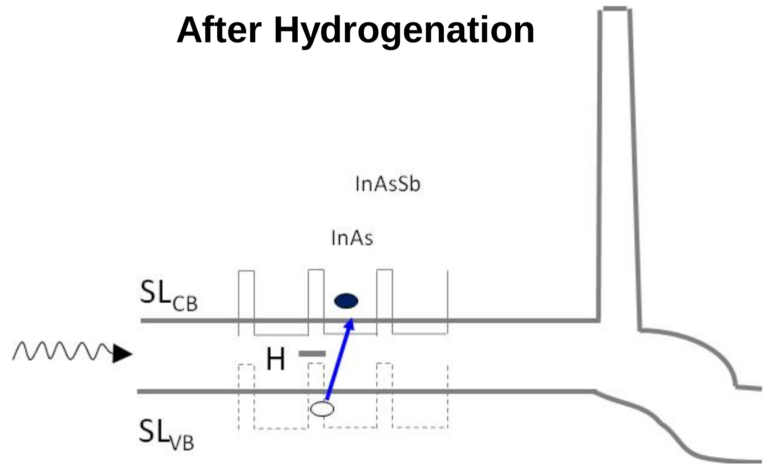
- Inductively coupled plasma (ICP) hydrogen can be introduced into molecular beam epitaxy (MBE) films, photodiodes, and detector arrays
- Dangling bonds around defects give rise to states in the band gap acting as SRH generation/ recombination centers.
- Hydrogen attaches to dangling bond, forms electrically inactive bonding and antibonding states
- Reducing the electrical activity of defects is equivalent to lowering the density of defects
- Innovative plasma-assisted hydrogenation technique may improve FPA performance:
  - Lower residual nonuniformity
  - Increased operability
  - Increased detectivity

Before Hydrogenation



Loss of photogenerated carriers through scattering and recombination

After Hydrogenation



Atomic hydrogen introduced by ICP renders inactive the scattering and recombination centers – *photocarriers are collected*

Hydrogenation of Semiconductors

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Hydrogenation of Si

- Locations in Si crystals:
  - Bound to a dangling bond at a defect site
  - Molecular hydrogen (H_2)
  - Atomic hydrogen (M site)
- Staebler-Wronski effect in polycrystalline solar cells
- Passivates impurities
- Deactivates donor and acceptors
- Si-H, Si-H_2, and Si-H_3 bonds on Si surfaces

Si Impurity susceptible to H^+/levels	E (eV)
Au, E(0.54) H(0.35)	2.3
Pd, E(0.22) H(0.32)	2.4
Pt, E(0.28)	2.3
Cu, H(0.20, 0.35, 0.53)	2.5
Ni, H(0.18, 0.21, 0.33)	2.5
Ag, E(0.54) H(0.29)	2.2
Fe, H(0.32, 0.39)	1.5
O-V, E(0.18)	1.9
V-V, E(0.22)	1.9
Laser, E(0.19, 0.3)	2.4
Sputter etching	1.8
Plastic deformation	3.1
Grain boundaries	2.5
Chalcogenides (S, Se, Te)	> 1.1

Hydrogenation of III-V Crystals

- Exceptional stability of the {Mg,H} pair has long prevented the p-type doping of GaN
- Hydrogen passivation of dislocation cores in GaN
  - Reduced leakage currents
  - Enhanced LED and laser diode performance
- Hydrogen passivates the prevalent (EL2) deep-level As anitisite (As_{Ga}) donor defects in GaAs, reducing compensation

Hydrogenation of Chalcogenides

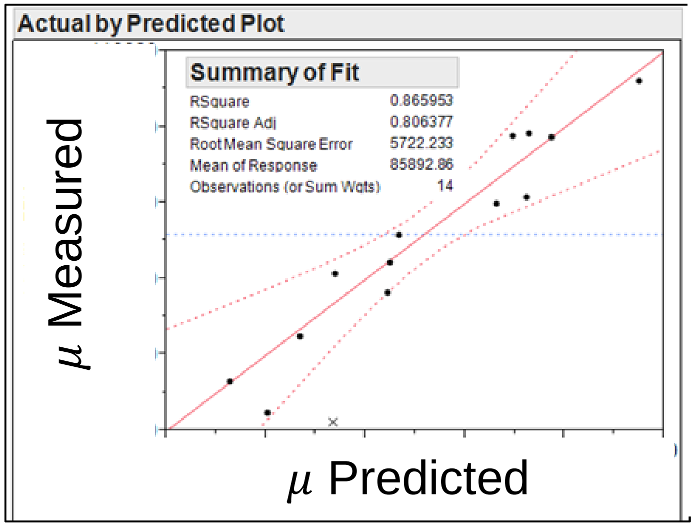
- Hydrogen in LPE HgCdTe reduces surface trap states and passivates Hg vacancies, but activity restored after 70^{o}C anneal
- Density functional theory predicts multiple hydrogen atoms attaching to a mercury vacancy; more likely than single atoms
- Cu, Ag, N_2 and Li in CdTe

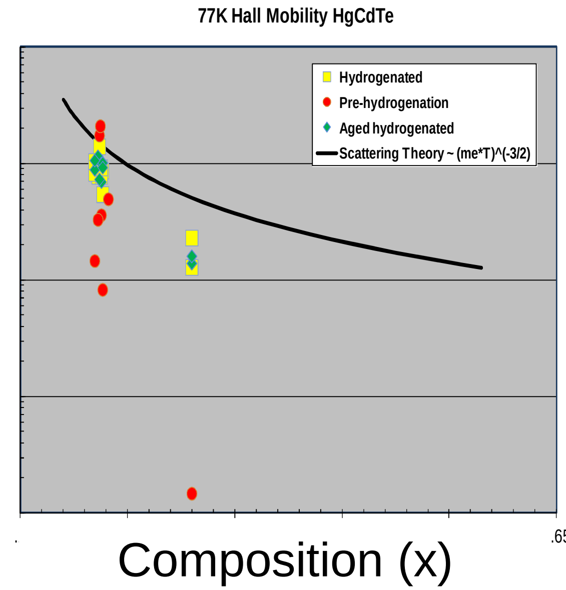
S.J. Pearton et al. “Hydrogen in Crystalline Semiconductors”, Appl. Phys. A 43, 153-195 (1987)

ICP Hydrogenation of HgCdTe

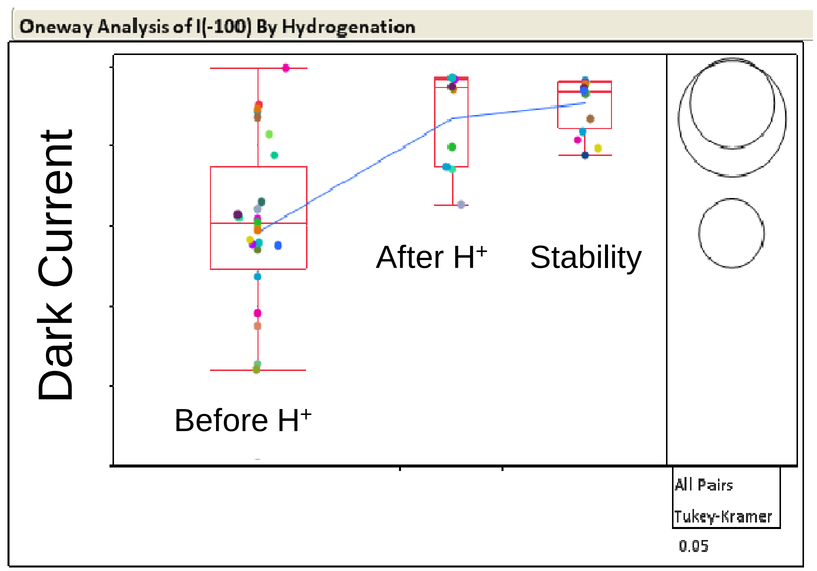
- Atomic hydrogen used in Si and GaAs
- Hydrogen passivation of dislocation cores in GaN reduces leakage currents and enhances LED and laser diode performance
- In HgCdTe: reduced surface trap states and passivated V_{Hg}
- Passivates deep defects, but restored after 70℃ anneal
- Prior work at EPIR Technologies:
  - H^+ reduces scattering and recombination in ICP exposed HgCdTe
- Photoassisted methods used for HgCdTe, but films and passivations degrade after UV exposure

Hall mobility analysis reveals key ICP parameters





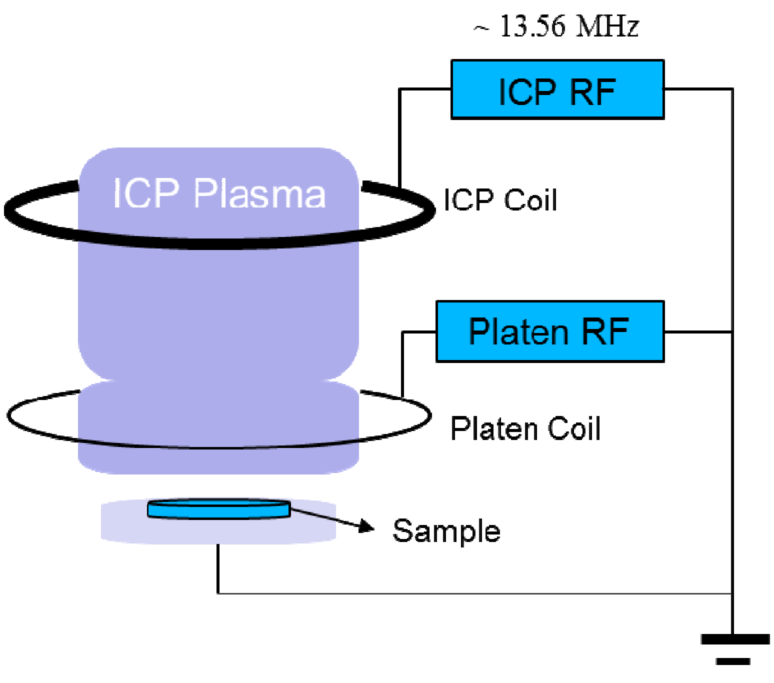
Dark current reduction after ICP hydrogenation



- Statistically significant improvements
- Stability tested over several months
- G-R and shunt components of dark current have been reduced
- Surface passivation improved

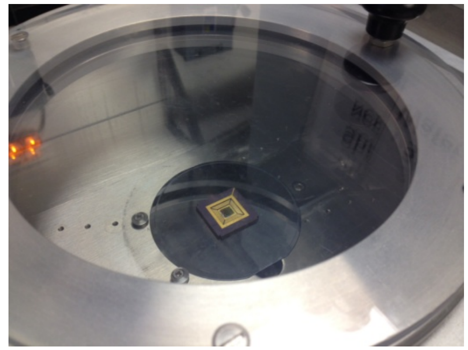
Technical Approach - Hydrogen Passivation Using ICP

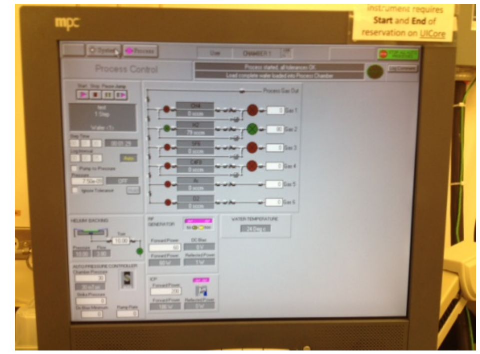
ICP schematic diagram



$H_2^+ + H_2 \rightarrow H_3^+ + H + 1.71\ \text{eV}$

- ICP ensures a high plasma density with a high density of atomic hydrogen at low operating pressures
- Additional bias can be applied to prevent ionized species from penetrating the sample





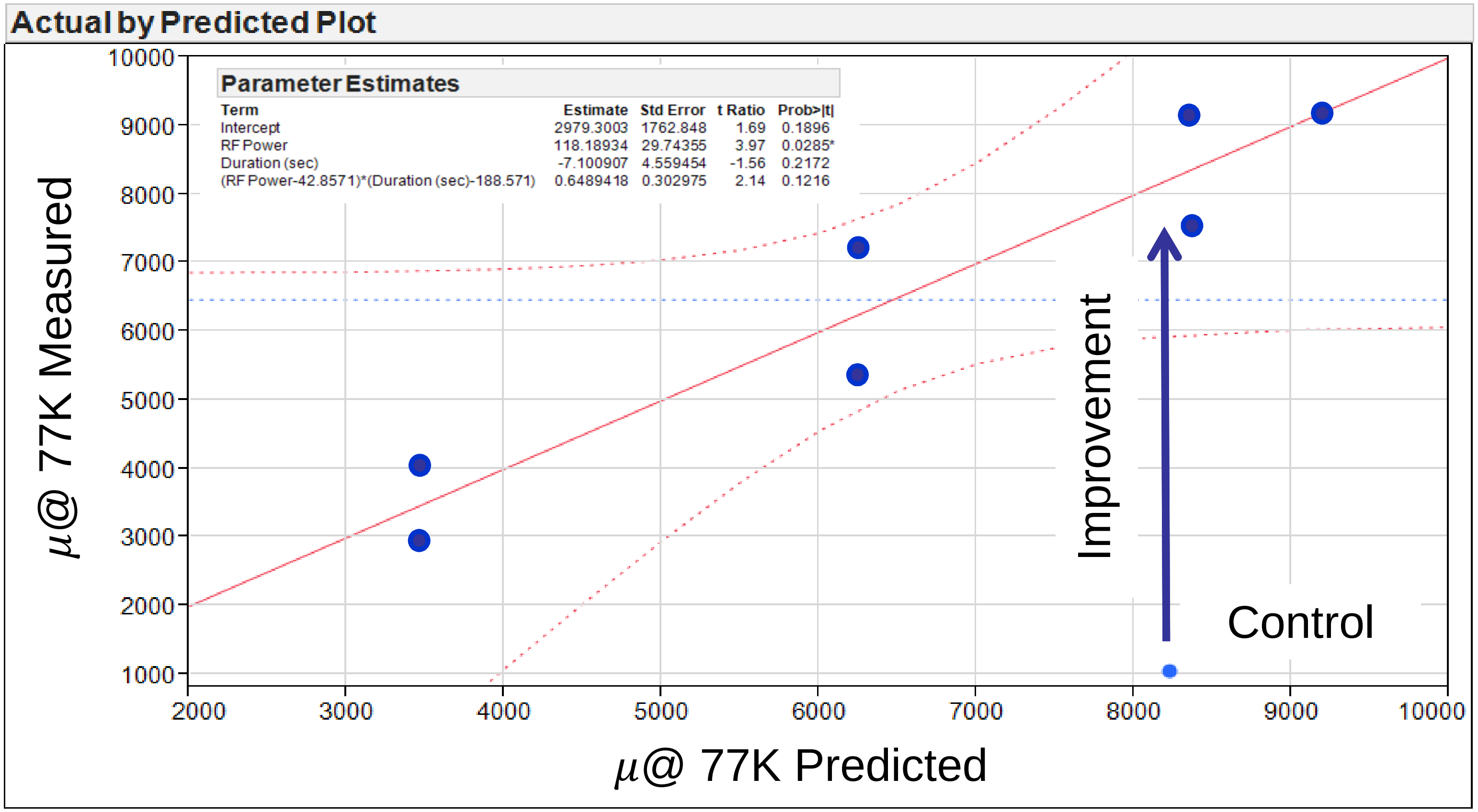
Approach

- **<u>Our goal:</u> Advance T2SL materials technology by passivating lifetime-limiting defects with H.**
- **Use ICP-generated atomic and ionized H diffused into T2SL films to passivate defects.**
- **Measure material properties (carrier mobility and lifetime) before and after ICP hydrogenation.**

Figures of Merit

- **Material-level metrics**
  - Minority carrier lifetime
  - Majority carrier mobility
- **Photodiode-level metrics**
  - I-V dark current – g/r, TAT, BTBT, diffusion
  - C-V sweeps - mobile charges, interface *n*
- **FPA-level metrics**
  - Noise equivalent temperature difference distribution
  - Pixel operability distribution

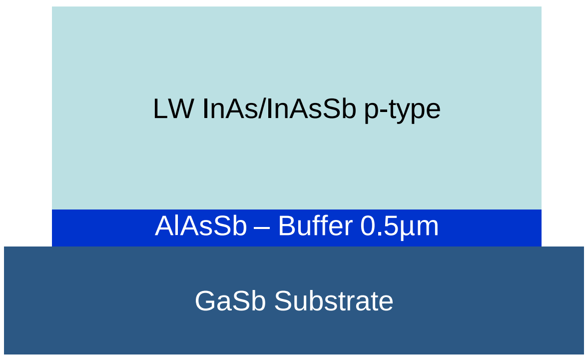
Preliminary T2SL Hydrogenation Results



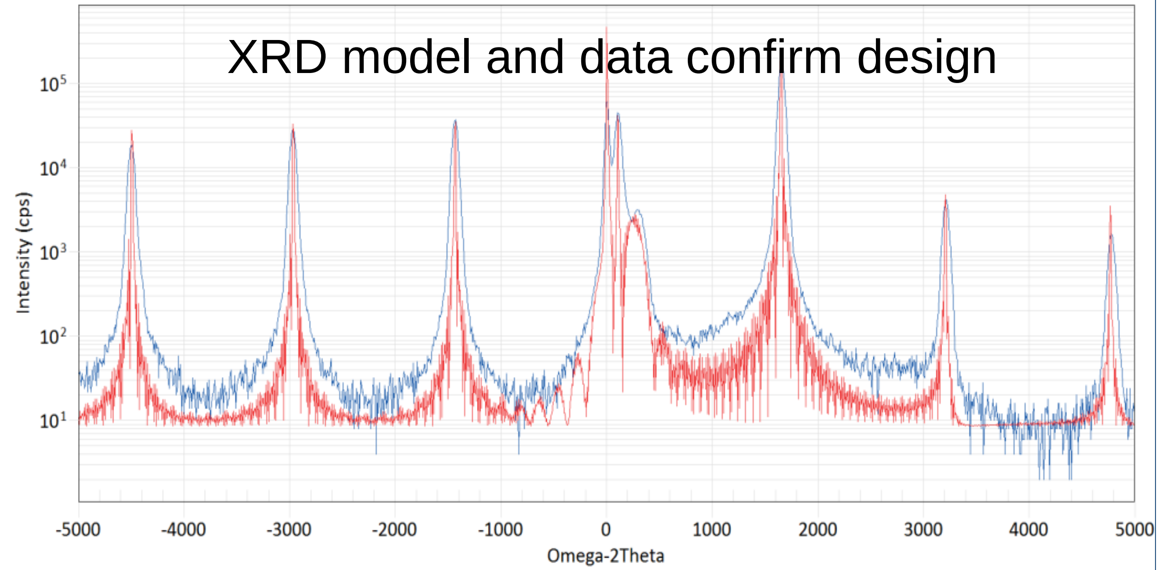
- Mobility increases with hydrogenation (79% adjusted R^2)
- Entirely a function of RF power and duration
  - Higher power, lower duration yields better μ
- Control sample shows far lower mobility

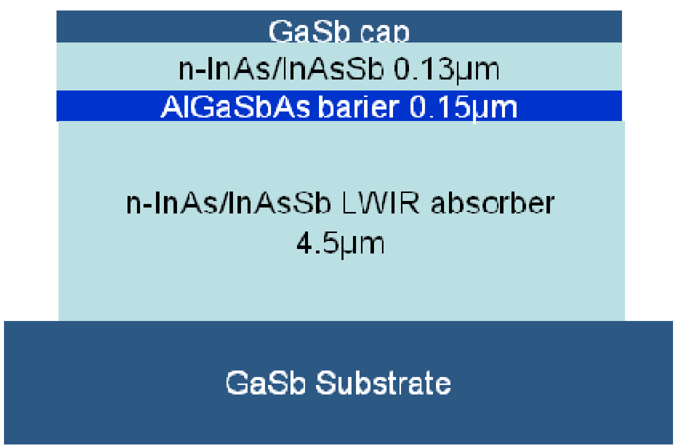
LWIR T2SL Material

4 µm 99Å InAs/34 Å $InAs_{0.59}Sb_{0.41}$, p~10^{15} cm^{-3}

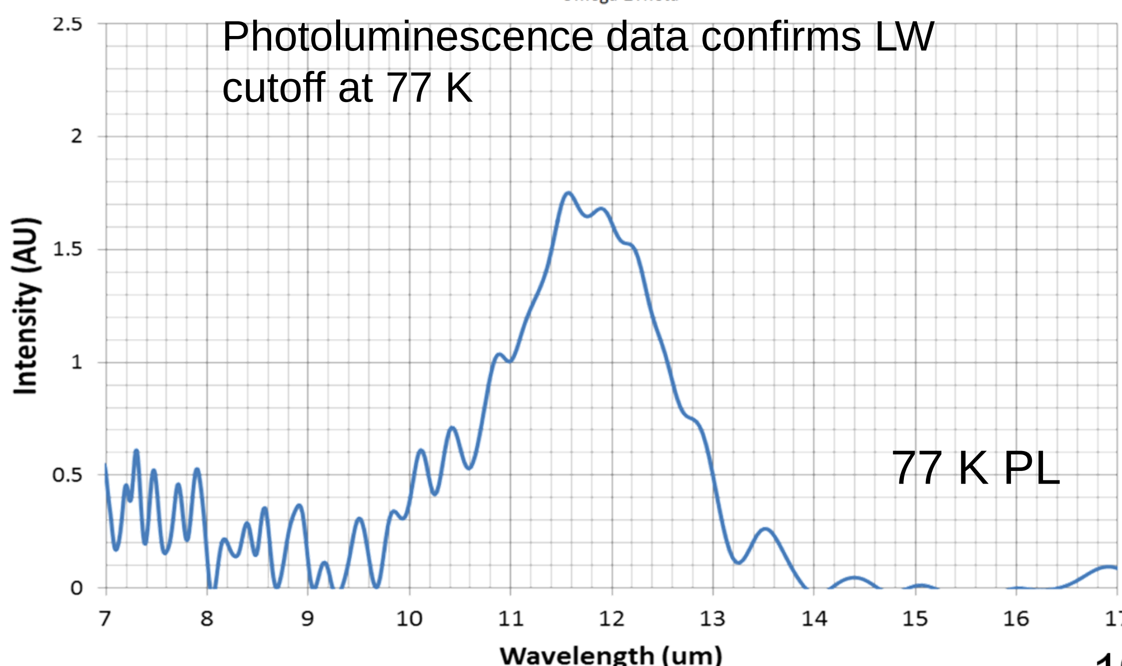


Acquired from IntelliEpi

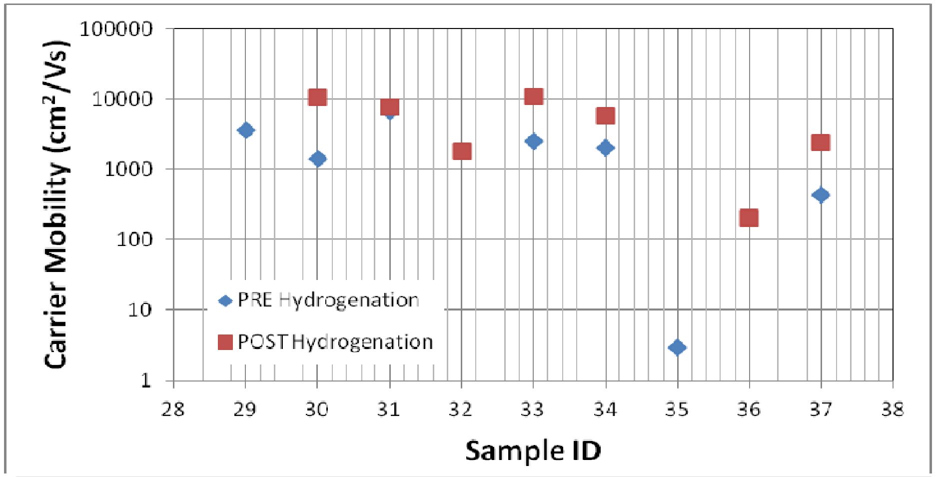




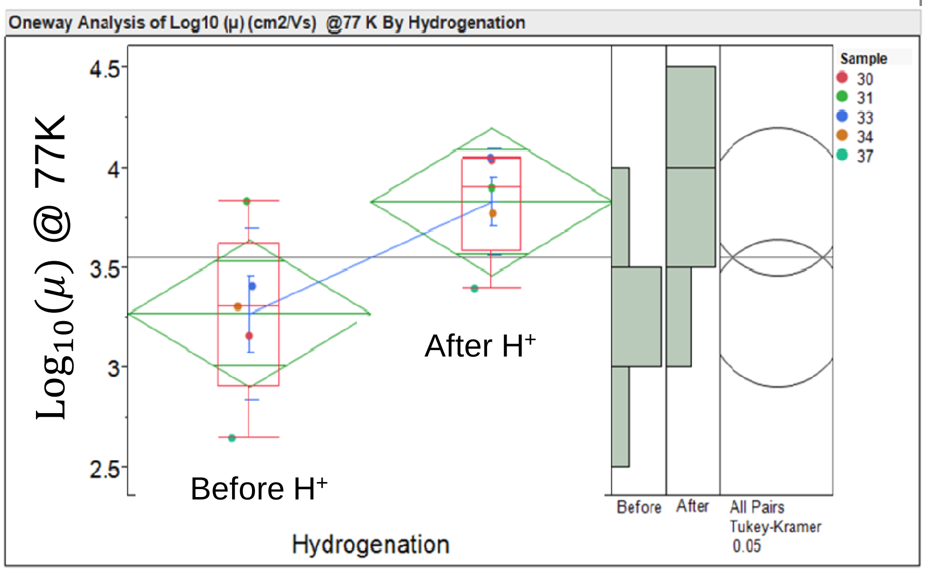
JPL-provided nBn detector structures

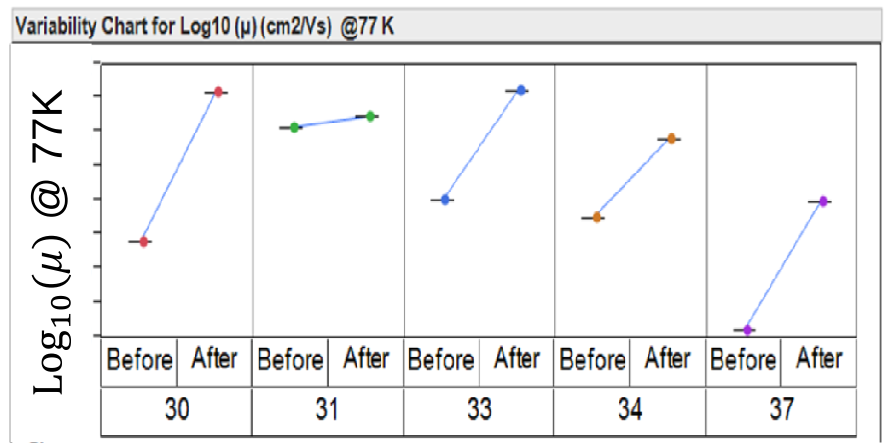


In-plane 77K Hall Mobility



Largest increases following hydrogenation from samples with lowest initial mobility values

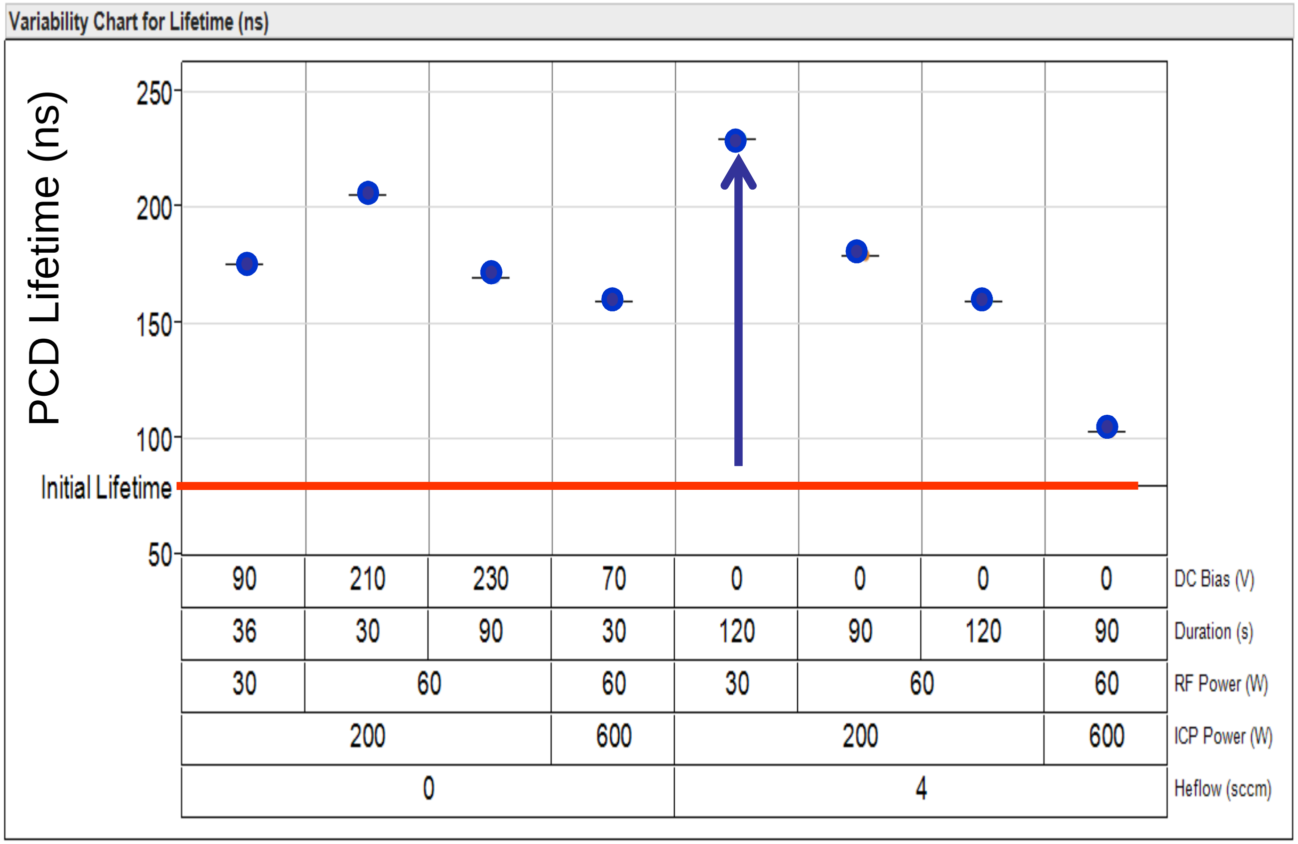




On average, mobility measured post-hydrogenation increased from 1800 cm^2/Vs to 6800 cm^2/Vs, a relative increase of over 300%

- Is statistically significant

Minority Carrier Lifetimes



Improved Hall mobilities following hydrogenation treatment using **<u>same</u>** plasma parameters that resulted in largest minority carrier lifetime increases

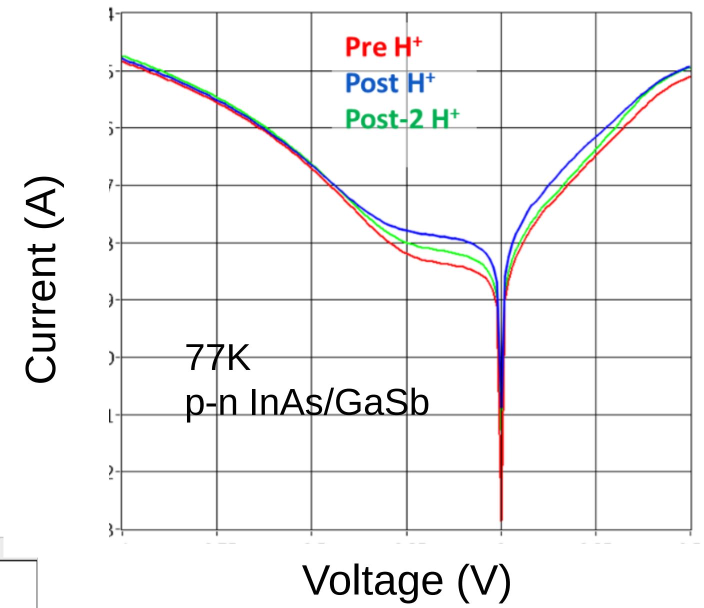
- ICP hydrogenation improved minority carrier lifetime for **<u>each</u>** of the ICP conditions explored
- Lifetime values have increased on the average from 80 ns, before hydrogenation, to over 200 ns, a relative increase of over 200%

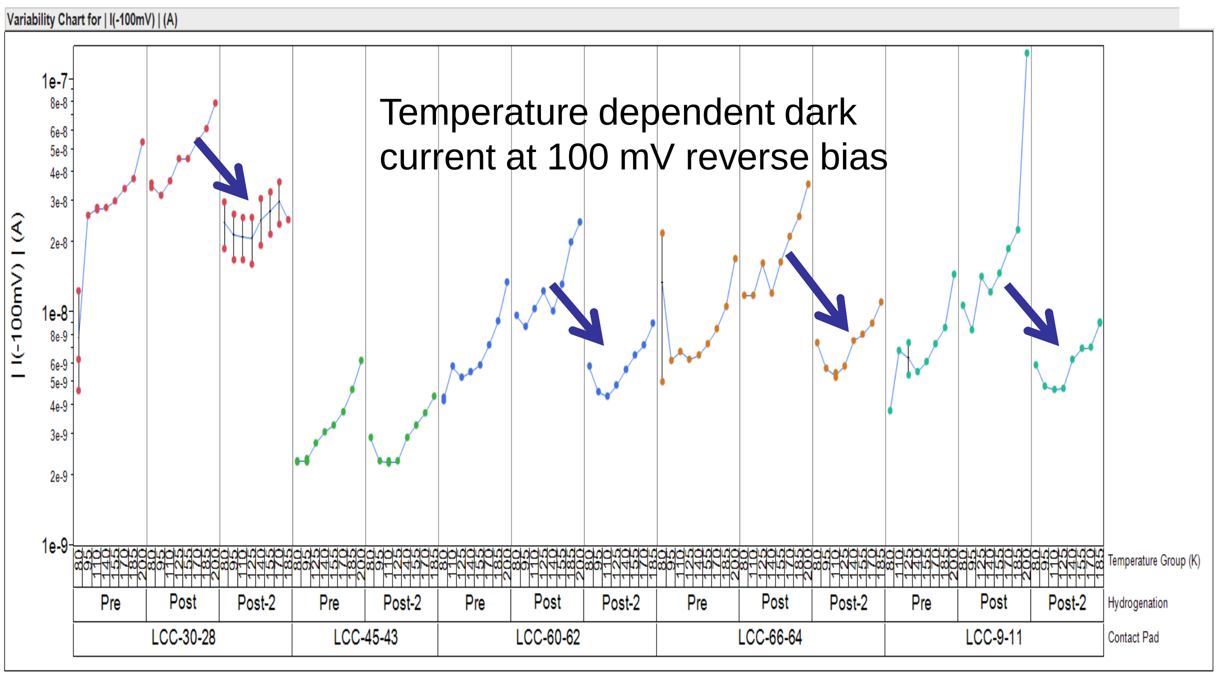
Dark Current Preliminary Study

Same photodiodes exposed twice

Hydrogenation 1: Lower DC biases – surface deterioration
Un-optimized process

Hydrogenation 2: Improved surface morphology
Improved dark current





ICP hydrogenation generates competing outcomes

Additional optimizations and trade-off studies required to enhance desired outcomes

Devices passivated with thioacetamide (TAM)

Statistical Analysis of Dark Currents

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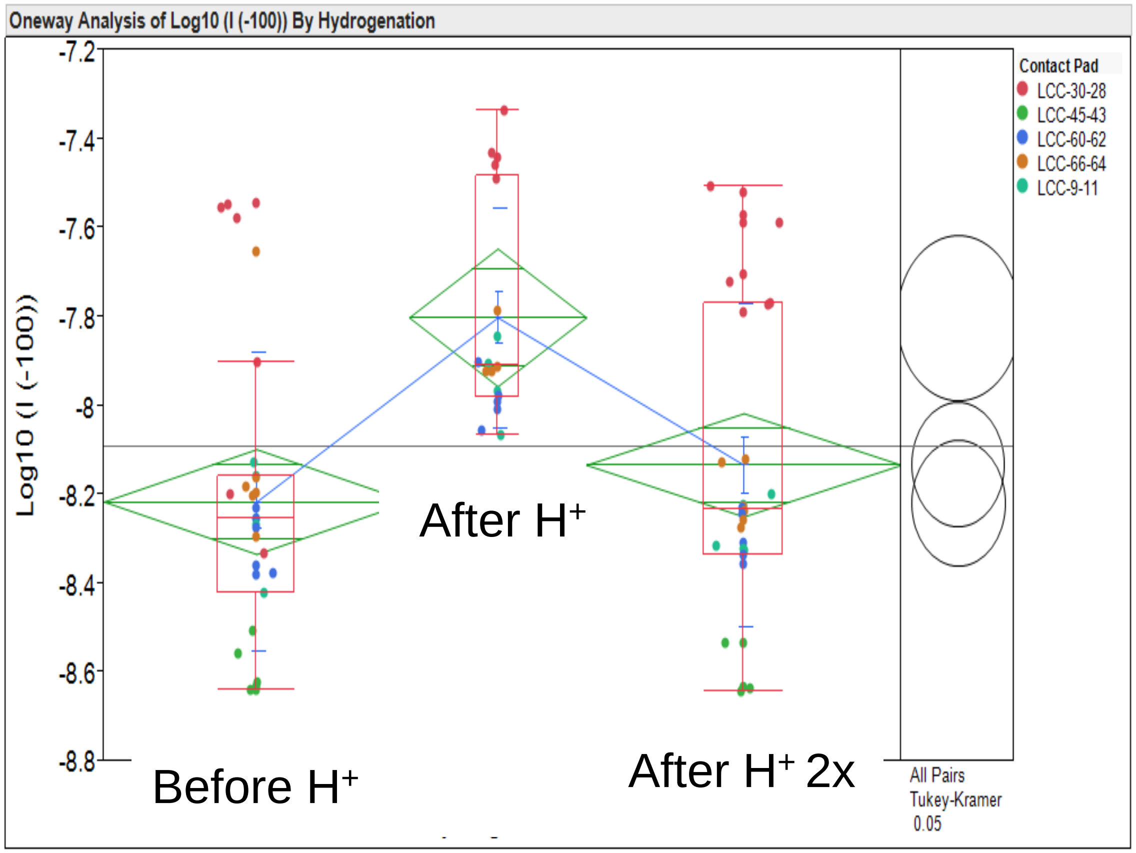


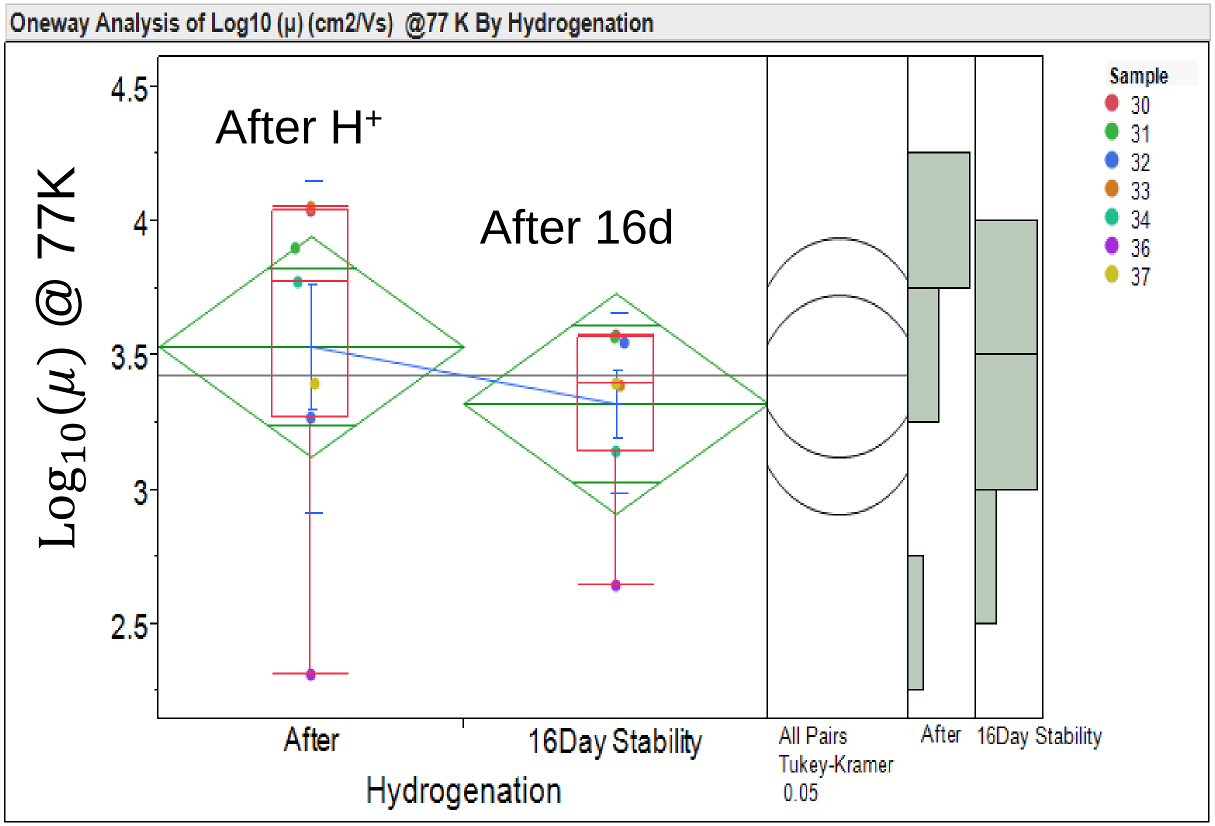
Although not optimal, the second ICP recipe is more beneficial than it is detrimental and has the potential to "repair" the material

Hydrogenation 2: same parameters produce largest mobility improvements measured on wafers

Some diodes were un-affected by ICP: contain different classes of defects

Second hydrogenation recipe has the potential to passivate at least some of material imperfections in general, not only those generated by an imperfect hydrogenation process

Mobility Stability of Hydrogenated T2SL



- In-plane 77 K Hall mobility
- Short term stability tested
- Room temperature storage
- No significant changes over couple of weeks

Summary

- ICP hydrogenation is a promising technique to advance state of the art large format T2SL FPAs
- At least partial passivation of recombination-mediating defects in T2SLs has been demonstrated (average ~200% increase in lifetime)
- Same ICP parameters increase in-plane mobility (average ~300% increase in 77K Hall mobility), and is stable over tested periods
- ICP hydrogenation has both beneficial and detrimental effects: need to further optimize

Potential Future Research

- Determine efficacy of hydrogen passivating various classes of defects (extended defects, localized defects, etc.)

- Explore and identify mechanisms of hydrogen diffusion
  - Exploit them to enhance retention of passivant and diffusion into desired locations, such as lateral diffusion to reach underneath metals in existing photodiodes

- Determine effect of hydrogen passivation on dopants and their electrical activity

- Determine the optimized plasma conditions for efficient passivation

- Explore the most suitable FPA fabrication step at which hydrogen passivation should be undertaken

- Explore long-term retention of hydrogenation benefits